DEPARTMENT OF TRANSPORTATION
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California Test 402
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METHODS FOR TESTING PAINTS AND RELATED MATERIALS

CAUTION: Prior to handling test materials, performing equipment setups, and/or conducting this method, testers are required to read "**SAFETY AND HEALTH**" in Part 10 of this method. It is the responsibility of whoever uses this method to consult and use departmental safety and health practices and determine the applicability of regulatory limitations before any testing is performed.

SCOPE

The procedures used for the chemical and/or physical testing of paints, varnishes, enamels, and the raw materials used in the manufacture of these organic protective coatings are described in this test method.

Samples of protective coatings submitted for analysis may be broadly classified as "field" samples and "stock" samples.

Stock samples from the manufacturer's batch of prepared material are drawn by State inspectors prior to shipment to the job. If the coating meets specifications, the inspector is notified that he may release the material. The number of tests performed on each sample depends upon several factors. Stock samples involving large lots are more extensively examined than are small batches.

Field samples are submitted by resident engineers from the job site where the coating is being used to determine if there has been any significant change in the product since it was released. Field samples are usually examined for only a few of the basic properties such as viscosity, weight per gallon, volatile content, drying time, and application. Such tests indicate if there has been any adulteration of the materials since leaving the factory.

Field samples may not always be representative of the material supplied as the possibility exists that the material was not thoroughly mixed before sampling. Test results on field samples must be evaluated with these factors in mind.

This test method is divided into the following parts:

1. Reagents
2. Paints and Enamels
3. Pigment Analysis
4. Raw Materials, Pigments
5. Resins
6. Solvents and Thinners
7. Drying Oils
8. Varnish
9. Aluminum Paste
10. Safety and Health

PART 1. REAGENTS

Unless otherwise indicated, all reagents shall conform to the specifications of the Committee on Analytical Reagents for the American Chemical Society, where such specifications are available.

PART 2. PAINTS AND ENAMELS

1. Condition in container: Refer to Method No. 3011 of Federal Test Method Standard 141.

2. Pigment - percent by weight:

   a. Extraction method: Follow ASTM D-2371, using appropriate amounts of paint sample and a suitable extraction mixture (a mixture or a single solvent which will be the best solvent for the resin components).

   b. Supercentrifuge method: Follow ASTM D-2698.

   c. Ignition method: Follow ASTM D-3723.

3. Density: Follow ASTM D-1475.

4. Volatile and non-volatile content: Follow ASTM D-2369 or D-3723.

5. Consistency (viscosity): Follow ASTM D-562.

6. Coarse particles: Follow ASTM D-185. For aluminum paste, follow ASTM D-480.

7. Dry opacity: On a black/white Leneta chart, Form 2A Opacity, draw down a film of the sample covering both black and white portions of the chart. Unless otherwise specified, use a 254 um gap draw-down blade. Dry the specimen 24 hours at 25˚C. Using a suitably calibrated filter photometer conforming to ASTM E-1347, measure alternately the 45˚/0˚ daylight luminous directional reflectance of the specimen over the white and black portions of the chart. Calculate dry opacity as follows:

   $$\text{Dry Opacity} = \frac{\text{Reflectance over black}}{\text{Reflectance over white}}$$

   Similar results may be obtained from spectrophotometers conforming to ASTM Recommended Practice E-308.

8. Dispersion (fineness of grind): Follow ASTM D-1210.

9. Gloss and reflectance: Refer to ASTM D-523 and E-1347. Use a suitable Gloss and Reflectance Meter.

10. Yellowness and accelerated yellowness: Refer to Federal Test Method Standard 141, Method Nos. 6131 and 6132.

11. Working properties: Follow Federal Test Method Standard 141, Method No. 4541.

12. Drying time, set to touch, dust free, etc.: Refer to ASTM D-1640.

    Usually, it is not necessary to draw down the film (bird doctor blade) for routine work, unless specified.

    For traffic paint Dry to No Pick Up without Beads, follow ASTM D-711. For traffic paint Dry Through Time, use the same draw down sample prepared for ASTM D-711. Perform the test as outlined in ASTM D-1640 except that no thumb pressure is used. The thumb is turned through an angle of 90˚ while in contact with the film. The time at which this rotation does not break the film is recorded.

13. Flexibility: Follow Method No. 6221 of Federal Test Method Standard 141, unless otherwise directed.

14. Adhesion: Follow ASTM D-3359, Method A or ASTM D-4541.

15. Gasoline and water resistance: Follow Federal Specification TT-E-489, unless otherwise directed.

16. Gel test: This procedure is mainly for State Specification paint, Vinyl Wash Primer. To 320-mL base resin in a 500-mL

can, add slowly and with constant stirring, 80-mL acid diluent. (Measuring of the components is easily done by using graduated paper cups.) Seal the can. Observe contents periodically for 24 hours. There shall be no gelling of the mix.

17. Organic chlorine content of vehicle: Supercentrifuge paint to remove pigment. Dry 1 to 2 grams of supercentrifuged vehicle for a minimum of 3 hours on a clean polytetrafluoroethylene sheet. Remove the dried vehicle and cut into small pieces (2 x 2 mm). Proceed with an oxygen bomb combustion as described in ASTM D-808. For routine work, the chlorine content following the combustion may be determined by a potentiometric titration. Acidify and filter the combustion solution as described in ASTM for a gravimetric determination, then proceed with a potentiometric titration using 0.1 normal silver nitrate. Monitor cell potential between a chloride specific ion electrode and double junction reference electrode. Refer to manufacturer's literature accompanying the electrodes for maintenance and specific operation procedures. Determine the equivalence point and calculate the chlorine content using the following:

$$\% \text{ Cl} = (\text{mL } AgNO_3) \text{ X } (\text{Normality of } AgNO_3 \text{ X } (.03545) \text{ X } 100/\text{Wt. of vehicle used}$$

18. Pencil hardness of paint films: Follow ASTM D-3363.

19. Percent water (Karl Fischer Method): Follow ASTM D-4017.

20. Infra red spectrum of vehicle solids: Follow ASTM D-2621 for solvent reducible paints and ASTM D-3168 for emulsion paints.

21. Analysis of paint solvents by gas chromatography: Follow ASTM D-3271, except use vehicle extracted by supercentrifuge in lieu of whole paint to inject into column.

22. Analysis of pigments in dried paint films by X-ray diffraction: Follow ASTM D-5380.

PART 3. PIGMENT ANALYSIS (Extracted Pigment)

1. Metallic zinc: Follow ASTM D-521.

2. Zinc pigments by the Ethylenediamine Tetraacetate Method: This can usually be used in place of a variety of older methods for determining Zn in the presence of Ca, Mg, Ba, Fe, Cr.

A. APPARATUS

1. Buffer solution (pH 10): Fifty-four g of ammonium chloride and 350 mL of concentrated ammonium hydroxide are diluted to 1 L of water.

2. Eriochrome Black T (0.5 %): Dissolve 0.25 g of Eriochrome Black T and 2.2 g of hydroxyl-amine hydrochloride (as stabilizer) in 50 mL of methanol.

3. Disodium ethylenediamine tetraacetate dihydrate 0.2 *N*: Dissolve 37.2 g of the reagent in water and dilute to 1 liter. Standardize against standard zinc oxide solution.

4. Standard zinc oxide solution: Weigh approximately 3 g of oven-dried zinc oxide of known purity and dissolve in the buffer solution. Then dilute to 500 mL with buffer.

B. PROCEDURE

1. Test a small amount of pigment for sulfides by the addition of dilute hydrochloric acid. If the odor of hydrogen sulfide is detected, the modified procedure is followed.

2. Procedure in Absence of Zinc Sulfide: Weigh approximately 1.000 g

of the isolated paint pigment into a 250-mL Erlenmeyer flask. If the sample is believed to contain more than 10 % zinc oxide, proportionately smaller samples may be used. Add 25 mL of the buffer solution, stopper the flask, and shake frequently and vigorously for 30 minutes. Filter into a 400-mL beaker. Wash the paper and flask well with distilled water. Discard the undissolved residue. Dilute the filtrate to 300 mL with water. Add ten drops of the Eriochrome Black T indicator and titrate with 0.2 *N* ethylenediamine tetraacetate solution. As it becomes apparent that the end point is near, add five more drops of indicator. In the absence of chromium, the color change at the end point is from wine-red to blue; if much chromium is present, the color change is from orange-red to green.

3. Procedure in Presence of Zinc Sulfide: Weigh approximately 1.000 g of the isolated pigment into a 250-mL beaker. Add 25 mL of 6 *N* hydrochloric acid. Heat gently for 30 minutes on a hot plate. Finally, boil without cover for a few minutes to expel the hydrogen sulfide. Cool, add 2 mL of 85 % phosphoric acid, followed by 35 mL of concentrated ammonium hydroxide and 25 mL of the buffer solution. The resulting mixture should be alkaline (approximately pH 10). Filter and wash well. Discard the paper and residue. Dilute the filtrate and titrate as above. Treat 25 mL of the standard zinc oxide solution in a similar manner, i.e., 2 mL of phosphoric acid, 25 mL of 6 *N* hydrochloric acid, 35 mL of concentrated ammonium hydroxide. Dilute and titrate as above. Calculation % zinc as:

   ZnO= (ml of reagent X normality of reagent X 4.069) / weight of pigment sample.

4. Zinc Yellow (Alternate Method).

   a. Determine total zinc by the ferrocyanide method and chromium by the dichromate method as specified in ASTM D-444. The extracted pigment from zinc chromate paint often resists wetting so that its solution by Method D-444 for chromium is difficult and may fail to give satisfactory results. The following method is rapid and gives accurate results:

      1. Dissolve 0.2 g of a detergent by heating with about 2 mL of distilled water in a 400 mL beaker. Wetting is more difficult if too much water is used.

      2. Weigh about 0.300 g of the finely ground pigment, transfer to the beaker containing detergent solution, and stir until all lumps are broken and the pigment is completely wet.

      3. Add 10 mL of 1:1 cold sulfuric acid, stir until the pigment is dissolved, and dilute to 250 to 300 mL with cold distilled water.

      4. Proceed with analysis for CrO_3 according to ASTM D-444.

5. Titanium Dioxide and Chromic Oxide in Ignited Pigment.

   Because it is not always possible to separate TiO_2 and Cr_2O_3 from paints by extraction, it becomes necessary to resort to ignition. Such ignited pigments are extremely resistant to solution by the usual methods. The following method gives accurate results with a minimum of difficulty.

   a. Weigh 0.200 g (more if a considerable amount of filler is present) of the ignited pigment and transfer to a 30 to 50-mL silver crucible.

   b. Add approximately 0.5 g of KNO_3 and 2 g of NaOH pellets.

c. Cover the crucible and heat at a low red heat for about 5 minutes, swirl occasionally.

NOTE: Silver melts at a bright red heat, 960˚C.

d. After cooling, place the crucible and its contents in a beaker of hot distilled water. Boil a few minutes, remove the crucible, and wash adhering TiO_2 and chromate into the beaker.

e. Allow the mixture in the beaker to settle and cool. Filter by suction through a glass filter paper in a Gooch crucible. If the mixture is not cold, suction may cause it to boil and some may be lost. Filtration is not difficult if the clear solution is carefully decanted into the filter, then the precipitate is transferred to the filter with a stream of hot water from the wash bottle. Wash the precipitate on the filter with hot distilled water.

f. Transfer the precipitate to a 250-mL beaker, using a minimum amount of wash water, and determine TiO_2 as specified in ASTM D-1394. Fifteen mL of H_2SO_4 is better than the 25 called for as the TiO_2 dissolves with little fuming.

g. Transfer the chromate solution from the suction flask to a 600-mL beaker; add 15 mL of 1:1 H_2SO_4 , 10 mL of 1:1 H_3PO_4 , and 10 mL of 1 % $AgNO_3$. Heat to boiling, remove from the hot plate, and while stirring carefully add about 2 g of ammonium persulfate. Boil a minute or two, remove from the hot plate and, again, add about 2 g of ammonium persulfate. Return to the hot plate and boil vigorously for at least ten minutes to destroy any remaining persulfate. Thorough oxidation of the chrome and also of KNO_2, which is present, is necessary. Any unoxidized KNO_2 will destroy the indicator which is used later.

h. Determine the Cr_2O_3 as specified in the Dichromate Method in ASTM D-444, except substitute barium diphenylamine sulfonate for orthophenanthroline.

6. Red Iron Oxide and Titanium Dioxide in Mixed Pigments

a. Isolation of Pigment:

Weigh 15 g of the thoroughly mixed paint into a large porcelain crucible and evaporate the volatile matter in a 100˚C oven. Then place crucible and contents in a 700˚C muffle furnace for at least two hours in order to completely destroy all organic matter. Transfer the pigment residue to a mortar and grind to a uniform product.

b. Separation of Pigment Components:

Weigh a 0.300 g sample of the pigment into a 600-mL beaker, add 30 mL of concentrated sulfuric acid and 30 mL of concentrated hydrochloric acid. Heat over a flame to copious SO_3 fumes, constantly swirling the beaker to prevent bumping. If there is any unreacted iron oxide residue in the bottom of the beaker, add an additional 30 mL of hydrochloric acid, and again heat to fumes until no black residue is noted in the bottom of the beaker. Add 8 g of ammonium sulfate to the beaker and fume again for several minutes. Cool the solution, dilute to about 300 mL, and heat for several minutes to obtain a clear solution. Add ammonium hydroxide until the solution is alkaline; then add 3 mL of 1:1 sulfuric acid. Dissolve 1.2 g of tartaric acid in the solution and pass a stream of hydrogen sulfide through it for several minutes until all of the

iron has been reduced to a ferrous state; this may be noted by the disappearance of the yellow color. Heat the solution to boiling, add an excess of ammonium hydroxide to precipitate the iron, and pass hydrogen sulfide through the hot solution for several minutes. Let the solution cool to room temperature and, again, saturate with hydrogen sulfide. Allow the precipitate to settle for a half hour and filter through a No. 41 Whatman filter paper. Wash the beaker and precipitate with a dilute solution of ammonium sulfide, made by passing hydrogen sulfide through dilute ammonium hydroxide. Save the filtrate for the titanium analysis.

c. Determination of Iron Oxide:

Place the filter paper and contents from the hydrogen sulfide precipitation in a 400-mL beaker; add 25 mL of concentrated hydrochloric acid, and macerate the paper with a stirring rod while heating the beaker to dissolve the ferrous sulfide. Dilute to about 250 mL and boil to remove hydrogen sulfide. Cool, add a few drops of barium diphenylamine sulfonate indicator, 10 mL of 1:1 phosphoric acid, and titrate with standard potassium dichromate solution 1 mL = 4.0 mg Fe_2O_3.
Percent Fe_2O_3 = 0.4 X mL $K_2Cr_2O_7$ solution / sample weight.

d. Determination of Titanium Dioxide:

Evaporate the filtrate from the iron precipitation to about 25 mL over a hot plate; direct a stream of air over the liquid surface to prevent bumping. Add 30 mL of concentrated sulfuric acid, heat to fumes, and add small amounts of nitric acid to completely destroy organic matter. Cool, wash sides of beaker with 3 to 5 mL of water, and heat to SO_3 fumes. Repeat, as necessary, with 3 to 5-mL portions of water to expel all nitrogen oxides. Cool, dilute, and proceed with the analysis of titanium as outlined in ASTM D-1394, Total Titanium by the Jones Reductor Method, beginning with the sentence: "Cool the solution, dilute with ...". Alternatively, determine the titanium dioxide content by Atomic Absorption Spectrometry following the procedures in ASTM D-4563.

7. Other Extracted Pigments:

Follow the analysis procedures in appropriate ASTM standards.

PART 4. RAW MATERIALS, PIGMENTS

1. Zinc pigments, general: Refer to Ethylenediamine Tetraacetate Method described under Section E, Pigment Analysis (Extracted Pigment).

2. Other pigment raw materials. Follow the analysis procedures in appropriate ASTM Standards.

PART 5. RESINS

Follow the procedures in appropriate ASTM Standards.

PART 6. SOLVENTS AND THINNERS

1. Specific gravity. Follow ASTM D-891.

2. Refractive index. Determine on a refractometer according to ASTM D-1218.

3. Distillation range. Follow ASTM D-86.

4. Evaporation rate. Follow ASTM D-3539.

5. Flash point. Follow ASTM D-3278.

6. Other properties. Follow the procedures of appropriate ASTM Standards.

PART 7. DRYING OILS

1. Specific Gravity: Follow ASTM D-1963.

2. Refractive Index: Determine on a Refractometer according to ASTM D-1218. Correct for temperature (+0.0004 per ° C above 25° C for tung oil and +0.00038 per degree C above 25° C for other oils).

3. Acid Value: Follow ASTM D-1639.

4. Saponification Value: ASTM D-1962.

5. Unsaponifiable Matter: Follow ASTM D-1965.

6. Viscosity: Follow ASTM D-1545.

7. Drying Time: Follow ASTM D-1640.

8. Iodine Value: Follow ASTM D-1541 or D-1959.

9. Other Properties: Follow the procedures of appropriate ASTM Standards.

PART 8. VARNISH

1. Non-volatile Content: Follow ASTM D-1644.

2. Drying Time: Follow ASTM D-1640 or Method No. 4061.2 of Federal Test Method Standard 141, except that film may be dipped.

3. Acid, Alkali, and Water Resistance:

   a. Thoroughly clean four 22 mm x 175 mm (approximate) test tubes in a neutral organic solvent, so that immersion in distilled water at room temperature will cause formation of a continuous water film upon withdrawal. After drying each tube, dip it into the sample of varnish, remove and immediately invert the mouth of the tube. Allow the varnish to dry for 95 hours in an atmosphere free of dust, drafts, products of combustion, or laboratory fumes. The temperature of the room during the drying period shall be 19 to 25°C (66° to 77°F). Refer to ASTM D-1647.

   b. Immerse the first varnish-coated test tube in boiling water for 7 hours, the second in 0.1 *N* sulfuric acid for 24 hours at 77° C, the third in 5 % sodium hydroxide solution for 6 hours at 25° C, and the fourth in water for 18 hours at 25° C. After the required immersion, rinse each tube thoroughly in running water, and allow to dry (at room temperature) for 30 minutes. Examine the varnish film on each test tube for any dullness, checking, or whitening.

   c. If test results are urgently needed, the immersion tests may be made after 48 hours air drying. However, the varnish cannot be rejected as failing these tests unless it undergoes the full 96-hour drying.

4. Kauri Reduction: Follow ASTM D-1642. Use Standard Kauri solution.

5. Viscosity: Follow ASTM D-1545.

6. Rosin: Follow ASTM D-1542, Liebermann-Storch Test.

7. Leafing Test for Mixed Paint: Mix Aluminum paste, 74 % non-volatile grade, in ratio of 100 grams per 417 mL of vehicle, brush out on a panel and examine for appearance and drying time. Dip a small tin-coated panel and examine for leafing properties. Refer also to the following Section K, Aluminum Paste.

8. Flash Point: Follow ASTM D-56 or D-3278.

PART 9. ALUMINUM PASTE

1. Leafing Properties: Follow ASTM Designation D-480. For comparative purposes on paste for a solvent borne paint, it will be sufficient to mix the paste with a suitable vehicle at the ratio of 100 g of paste per 417 mL of vehicle. For comparative purposes on paste for a waterborne paint, mix 0.1 g of paste with 10 mL of water. Leafing grade paste will

uniformly cover the water surface with a reflective film of aluminum. See also Leafing Test for Mixed Paint under preceding Section J, Varnish, Aluminum Vehicle.

2. Other Properties: Follow ASTM D-480.

PART 10. SAFETY AND HEALTH

This method may involve hazardous materials, operations, and equipment. This method does not purport to address all the safety problems associated with its use. It is the responsibility of whoever uses this method to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. Users of this method do so at their own risk.

While using these procedures, personnel shall comply with the requirements for Safe Laboratory Practices contained in the California Department of Transportation's Laboratory Safety Manual. Specific precautions will vary depending on the particular procedure performed, but will at the minimum require proper laboratory clothing, safety glasses and protective gloves. Paints and related materials that are tested may also have hazardous properties. Prior to handling any coating or related materials, personnel are required to consult the manufacturer's material safety data sheet (MSDS) for the materials and follow all precautions that are outlined.

REFERENCES:

ASTM Standards on Paint, Varnish, Lacquer, and Related Products
Federal Test Method Standard 141
Federal Specification TT-E-489.

End of Test (California Test 402 contains 8 pages)